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INFLUENCE OF IODINE VALUE ON COMBUSTION AND NO_X EMISSION CHARACTERISTICS OF A DI DIESEL ENGINE

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ABSTRACT

Biodiesel is a renewable fuel that has been shown to reduce many exhaust emissions, except oxides of nitrogen (NOx), in diesel engine cars. This is of special concern in inner urban areas that are subject to strict environmental regulations, such as EURO norms. Also, the use of pure biodiesel (B100) is inhibited because of its higher NOx emissions compared to petroleum diesel fuel. The aim of this present work is to investigate the effect of the iodine value and cetane number of various biodiesel fuels obtained from different feed stocks on the combustion and NOx emission characteristics of a direct injection (DI) diesel engine. The biodiesel fuels were chosen from various feed stocks such as coconut, palm kernel, mahua (*Madhuca indica*), pongamia pinnata, jatropha curcas, rice bran, and sesame seed oils. The experimental results show an approximately linear relationship between iodine value and NOx emissions. The biodiesels obtained from coconut and palm kernel showed lower NOx levels than diesel, but other biodiesels showed an increase in NOx. It was observed that the nature of the fatty acids of the biodiesel fuels had a significant influence on the NOx emissions. Also, the cetane numbers of the biodiesel fuels are affected both premixed combustion and the combustion rate, which further affected the amount of NOx formation. It was concluded that NOx emissions are influenced by many parameters of biodiesel fuels, particularly the iodine value and cetane number.

Keywords: Biodiesel feed stocks, Iodine value, Cetane number, Bulk modulus, Diesel engine combustion, NOx.

INTRODUCTION

Petroleum products, the actual base of the world energy matrix, are causing serious problems to the environment. In particular, diesel engine emissions irritate the eyes and throat, reduce the ability of blood to carry oxygen to the brain, and pass deep into the lungs causing respiratory problems for human beings. One way of reducing these engine emissions is to use oxygenated fuels such as biodiesel. As a potential alternative fuel source, biodiesel is currently being considered world-wide for use in diesel engines. Although the use of biodiesel offers many environmental advantages over petroleum diesel (PD), an increase in NOx emissions from biodiesel combustion, relative to levels observed from PD combustion, has been reported by several researchers (Spataru et al., 1995; Staat et al., 1995; Grabowski et al., 1998; Choi, et al., 1999; Song et el., 2002; Raheman et al., 2004; Nabi et al., 2006). This increase is of concern in areas that are subject to strict environmental regulations. If biodiesel is to be accepted universally, it is desirable both to reduce these NOx emissions at least to levels observed with PD combustion and to identify feed stocks which may produce lower NOx than PD combustion.

For this study, seven biodiesels were selected to represent a wide range of iodine values and cetane numbers for which the determination of NOx formation is important. Thus first generation biodiesel fuels obtained from edible feedstocks such as coconut, rice bran, and used sesame seed oil, and second generation biodiesel fuels obtained from non-edible feed stocks such as palm kernel, mahua, pongamia pinnata, and jatropha curcas oils were selected.

PROPERTIES OF BIODIESEL FUELS

The transesterification of vegetable oil with methanol yields mono-alkyl esters, which are defined as biodiesel. Therefore, biodiesel can be termed as the mixture of fatty acid methyl esters with each ester component contributing to the properties of the fuel. The structural features that influence the physical and chemical properties of a fatty ester molecule are chain length, degree of unsaturation, and branching of the chain (Knothe & Steidley, 2005).

Fatty acid composition

The performance of an ester as diesel fuel depends on the chemical composition of the ester, particularly the carbon chain length and the degree of saturation and unsaturation of the fatty acid molecules (Knothe & Steidley, 2005). The feed stock dependent fatty acid composition (hydrocarbon chains) varies from C_8 to C_{24} for the selected biodiesel fuels (White1980; Apple, 1980; Gunstone 1994; Rafel; Shasikant 2005; Vigya Kesari et al. 2010), shown in Fig.1

Fatty acids that do not contain double bonds are referred to as saturated because they contain the maximum number of hydrogen atoms that a carbon molecule can hold. Fatty acids that contain one double bond are called monounsaturated (MUFA), while fatty acids that contain two or more double bonds are called polyunsaturated (PUFA). The coconut oil methyl ester (COME) consists of 91% saturated fatty acids (SFA), while the sesame seed methyl ester (SSME) consists of just 13% (Refael, 1990; Apple, 1980; Gunstone et al., 1994). The pongamia pinnata oil methyl ester (POME) has the highest percentage of MUFA (55%), and the SSME contains the highest percentage of PUFA (45%), as shown in Fig.2 (Raheman & Phadatare, 2004; Knothe & Steidley, 2005). The kinematic viscosities of fatty acids are shown in Fig. 3. The viscosity increases with chain length and decreases with branching.

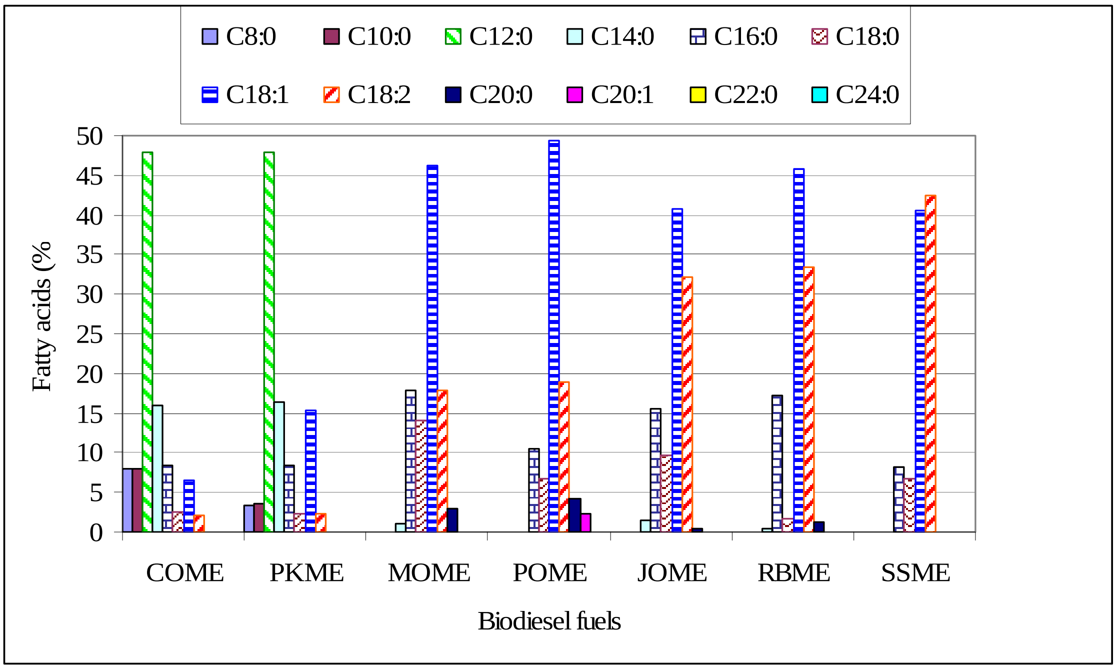


Fig.1: Types of fatty acids in various biodiesel (FAME) fuels

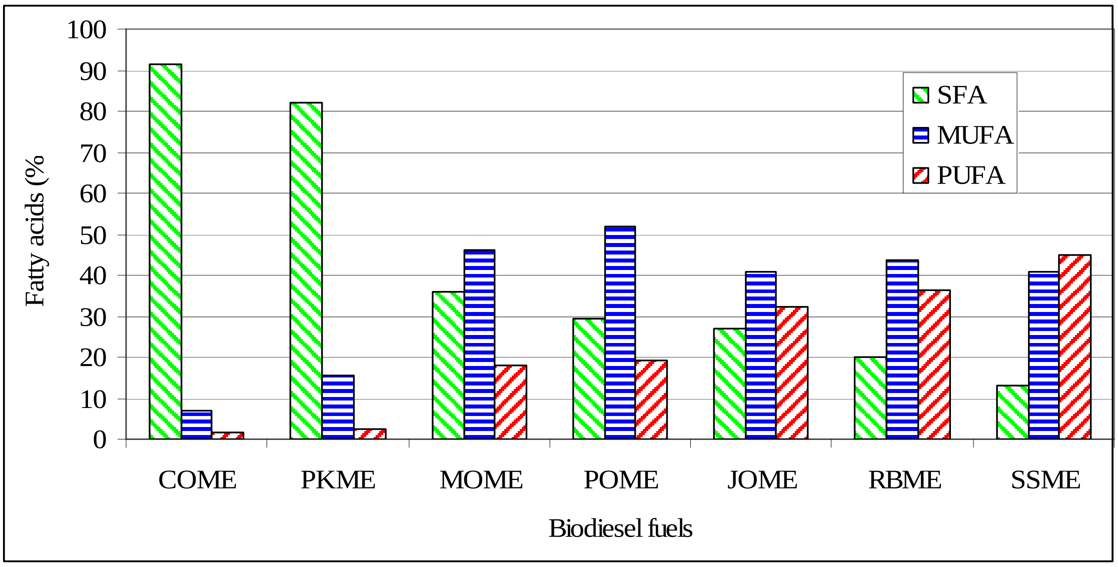


Fig.2: Saturated and unsaturated fatty acids in biodiesel fuels

Cetane number

The cetane number (CN) is an indicator of the ignition quality of the diesel fuel. It is related to the ignition delay (ID) time, i.e., the time that passes between injection of the fuel and onset of ignition. A shorter ID corresponds to a higher CN and vice versa. The standard ASTM D975 (American Society for Testing and Materials**:** D975) for conventional diesel fuel requires a minimum CN of 40 while the American standard for biodiesel prescribes a minimum CN of 47 (ASTM D6751). The CN of biodiesel fuels depends on the feedstock; it decreases as chain length decreases and branching increases or the CN increases with chain length, and decreases with the number and location of double bonds (Knothe, 1998) as shown in Fig.4. Also, the straight-chain, saturated hydrocarbons have higher CNs than the branched-chain of similar molecular weight and number of carbon atoms. The longer the fatty acid carbon chains and the more saturated the molecules, the higher the CN. Cetane numbers of selected biodiesels increase from 52 to 65, as shown in Fig. 5 (Refael, 1990; Heinrich Prankl et al. 1999; Adebowale & Adedire, 2006).

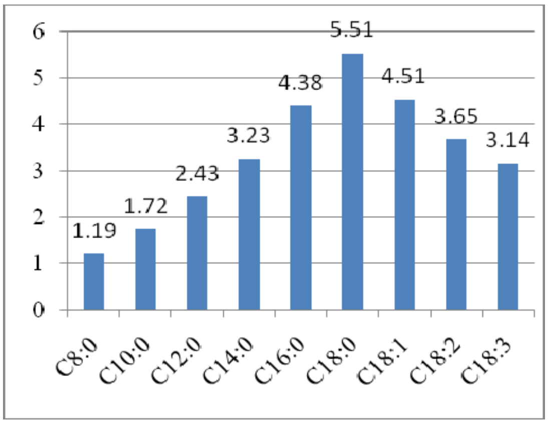


Fig. 3: Kinematic viscosity (cSt) of fatty acids

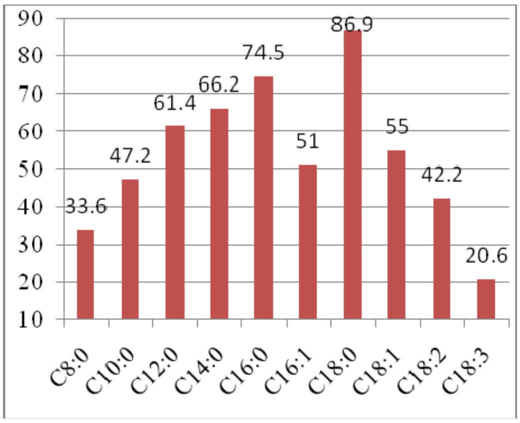


Fig. 4: Cetane numbers of fatty acids

Iodine value

The iodine value (IV) is one of the most commonly applied indices in fatty acid chemistry and is useful for analyzing fats and oils and describing their structure property relationships. Iodine value is used to compare the number of C=C contained in natural complex mixtures of fatty acid alkyl esters. This is a measure of the unsaturated fatty acid content and indicates the ease of oxidation of the product. The higher the iodine value, the higher the unsaturation degree, meaning a higher number of double bonds in the biofuel (Heinrich, 1999). Iodine values are useful for determining the overall degree of saturation of the oil, which is important for viscosity and cloud points. The lower the iodine value, the better the fuel will be as a biodiesel. Biodiesel from vegetable oils with high amounts of saturates (which means low IVs) will have a higher CN, while biodiesel from vegetable oils with high amounts of unsaturates (high IVs) will have a lower CN. Unsaturation in the fatty acid chain is the most significant cause of lower cetane numbers. Iodine values greater than 50 may result in decreased engine life, but give better viscosity characteristics in cooler conditions (Caye, 2008).

The ASTM establishes a maximum limit for the iodine value of biodiesel samples, since a high iodine value indicates a higher potential for biodiesel degradation, either through thermal oxidation or free radical attack. In the European standard, the maximum IV of biodiesel is 120, which excludes soybean oil methyl ester as a biodiesel fuel. Iodine value is included in biodiesel standards in order to limit the propensity for the oxidation of the biodiesel, which is especially characteristic of polyunsaturated fatty acids, and to reduce engine deposits traceable to double bond polymerization. Iodine values of selected biodiesel fuels are shown in Fig. 6.

Iodine values are determined by the Wijs method. The amount of the oil sample to be weighed was known from the following Tab. 1, as it depends on the iodine value of the sample. The oil sample was weighed into a dry iodine flask and was dissolved by the addition of 15 mL of carbon tetrachloride (CCl_4) and 20 mL of Wijs solution (iodine monochloride in glacial acetic acid) was added. The mixture was allowed to stand in the dark for 30 minutes at temperature of 15-25 ^oC. The 20 mL of potassium iodide solution was added to the flask. The flask was then shaken and the contents were titrated with sodium thiosulphate solution using starch as an indicator. The experiment was also carried out without the oil to obtain a blank value. The iodine value (IV) of the sample was calculated by using the formula: IV = 12.69 M (B-A)/W, where, A is the volume (mL) of sodium thiosulphate solution consumed for the sample, B is the volume (mL) of sodium thiosulphate solution consumed for the blank value, M is the concentration of sodium thiosulphate solution (moles L^{-1}), and W is the weight of the sample in grams. The lower the IV the higher the CN as shown in Fig. 5 and Fig.6.

Tab. 1: Iodine value (IV) and sample weight

Iodine value	Weight of sample (g)	Accuracy of weighing (mg)
5-20	1.0	1.0
20-60	0.34	0.1
60-80	0.25	0.1
80-130	0.15	0.1

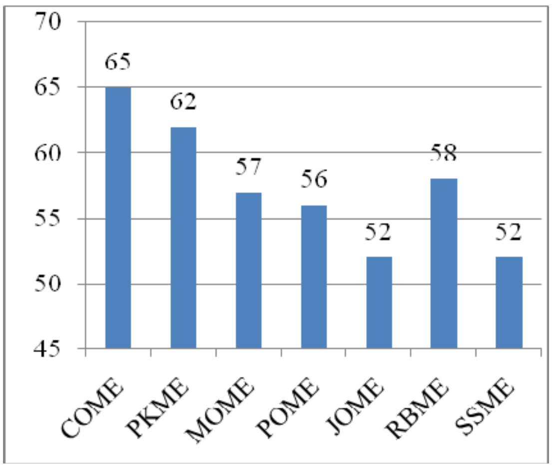


Fig.5: Cetane numbers of biodiesels

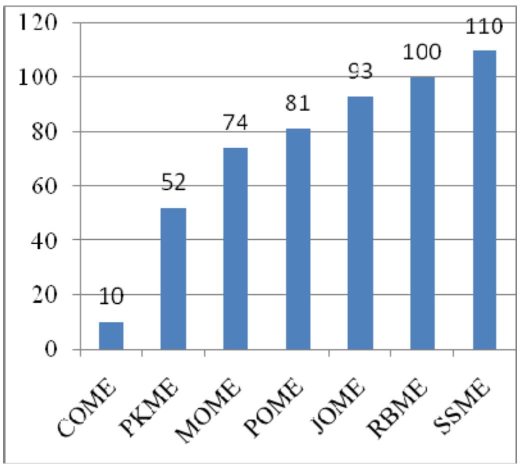
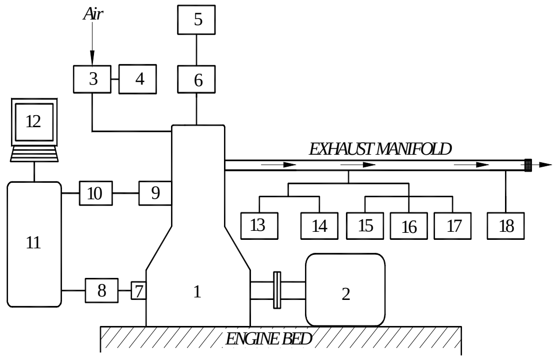


Fig.6: Iodine values of biodiesels

EXPERIMENTATION

The experiments were performed on a 4-stroke cycle, naturally aspirated, single cylinder, direct injection diesel engine (shown in Fig. 7), with the specifications shown in Tab.2. This engine employs a traditional, cam-driven, in-line fuel injection system. The fuel injection was performed at a static injection timing (optimum) of 23^{o} BTDC set for PD fuel.



1. DI-CI Engine (Kirloskar AV1), 2. Eddy Current Dynamometer, 3. Air Box, 4. U-Tube Manometer, 5. Fuel Tank, 6. Fuel Measurement, 7. TDC Postion Sensor, 8. TDC Amplifier Circuit, 9. Pressure Sensor, 10. Charge Amplifier, 11. Data Logger, 12. Computer, 13. HC Analyzer, 14. NO_x Analyzer, 15. O_2 Analyzer, 16. CO Analyzer, 17. CO_2 Analyzer, 18. Bosch Smoke Meter

Fig. 7: Layout of engine test rig

Tab.2: Technical data of engine test rig

Engine make and model	Kirloskar-AV1,India
Maximum power output	3.72 kW
Rated speed (constant)	1500 pm
Bore x stroke	80 mm x 110 mm
Compression ratio	16.5
Fuel injection system	In-line, direct injection
Nozzle opening pressure	205 bar
Method of cooling	Water cooling
Brake mean effective pressure @ 1500 rpm	5.42 kg/cm^2

Tests were carried out on the test rig with baseline PD and biodiesel fuels obtained from vegetable oils of seven different feedstocks: coconut, palm kernel, mahua (*Madhuca indica*), pongamia pinnata, jatropha, rice bran and sesame seed with an iodine value of 10 to 110. An eddy current dynamometer was used to measure the power (or torque) and the brake load was varied in five equal steps. Apex innovations (Pune, India) software C7112 was used to record the combustion pressure in the engine cylinder. An M RU exhaust gas analyzer (model: Delta 1600 L) was used to measure the NOx emissions.

COMBUSTION AND NOx FORMATION

The formation of NOx is dependent on the temperature during combustion, the amount of O_2 and N_2 in the charge, and the time available for them to react with each other in the engine combustion chamber. The combustion process in diesel engines is mainly divided into three phases as shown in Fig. 8. The first phase is called ignition delay (ID), which is the time period between the start of injection (SOI) and the start of combustion (SOC). In this period, the tiny fuel droplets evaporate and mix with high temperature (or high pressure) air. The delay period depends mainly on the fuel CN and the temperature of the air. The second phase is called the period of rapid combustion or premixed combustion. In this phase the air fuel mixture undergoes rapid combustion therefore, the pressure rise is rapid and releases maximum heat flux. The fuel droplets injected during the second phase burn faster with reduced ID due to the high temperature and pressure. In the third phase the pressure rise is controlled by the injection rate and the combustion is in diffusive mode.

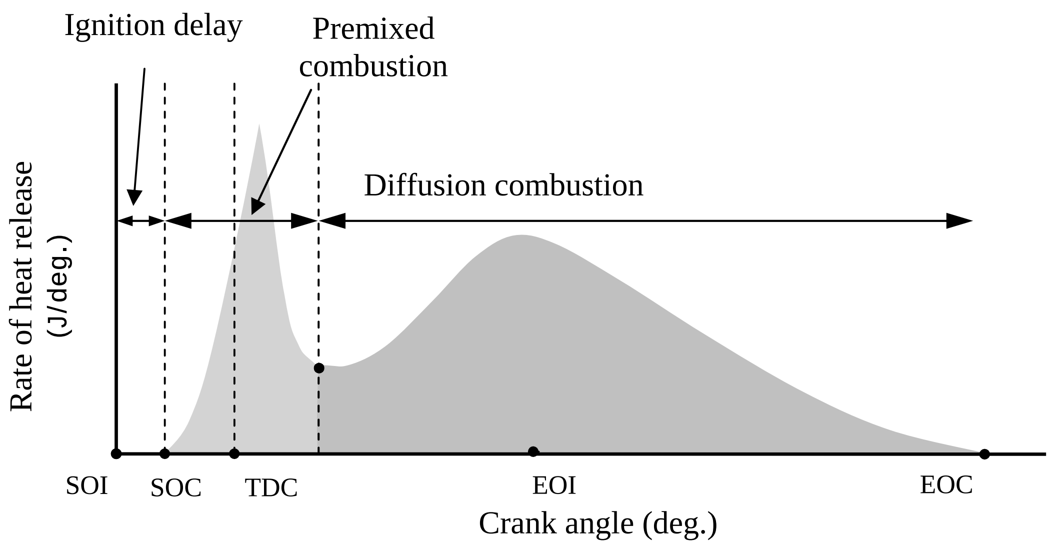


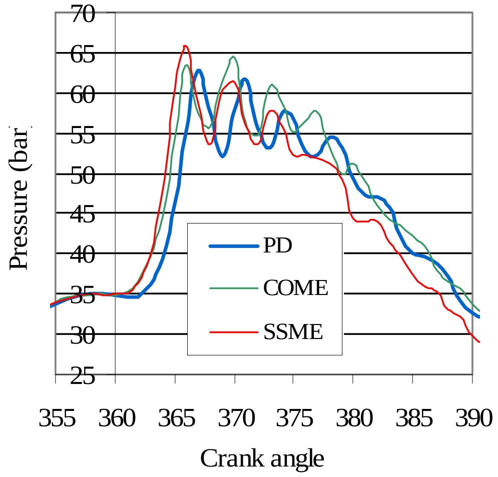
Fig. 8: Combustion phases in a diesel engine

NOx can be formed by two pathways during petroleum diesel combustion: the Fenimore (prompt) mechanism and the Zeldovich (thermal) mechanism. The rate of Zeldovich reactions is flame temperature-dependent, whereas the Fenimore pathway is more complex. In the Fenimore mechanism, free radicals formed from the fuel react with N_2 to eventually form NOx. This takes place very early in the combustion process and is partly dependent upon the fuel radical concentration and how it is established (Miller & Brown, 1989).

RESULTS AND DISCUSSION

Combustion analysis

From Fig. 9 and Fig. 10, it is observed that the biodiesels burn close to top dead centre (TDC) and their peak pressures are higher than that of petroleum diesel. This is attributed to the high density of the biodiesels. When a high density fuel is injected, there is an early lift of the needle in the nozzle, causing an advanced injection; and hence the combustion takes place near TDC. Correspondingly, the peak pressures of the biodiesel fuels are higher than that of PD, as shown in Fig. 9. The advanced combustion timing can result in higher combustion temperature and higher NOx emission due to the Zeldovich (thermal) mechanism. The peak pressure depends on the combustion rate in the initial phase, which is influenced by the fuel taking part in the premixed combustion phase. Once the auto-ignition of the fuel commences, the cylinder pressure rises, leading to the premixed combustion phase. The premixed (or rapid) combustion of SSME is higher than that of PD fuel. This is attributed to the combined effect of advanced injection and lower heat rejection value, due to the smaller cylinder volume (or surface area) near the TDC. Therefore, the high density of biodiesel fuels leads to more NOx.



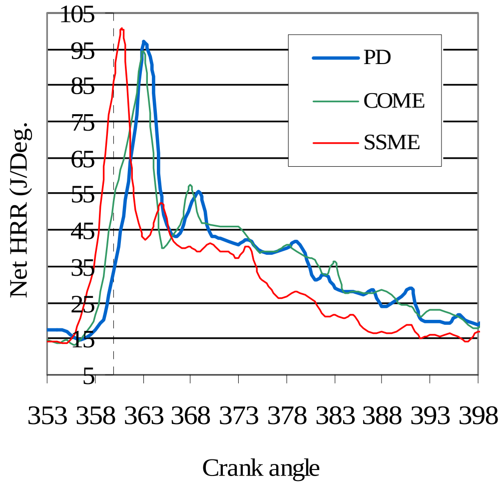


Fig. 9: Pressure vs. crank angle

Fig.10: Pressure vs. net heat release rate (HRR)

NOx analysis

The NOx emissions from seven biodiesels, from 0.93 kW to 3.72 kW, are illustrated in Fig.11. Results show that, for all the fuels, the increased power output promotes NOx emission. Since the formation of NOx is very sensitive to temperature, these higher power outputs promote cylinder charge temperature, which is responsible for the Zeldovich (or thermal) NOx formation. The NOx emissions from COME and PKME are lower and those from MOME, JOME, RBME and SSME are higher than with PD fuel. However, the NOx emission differences between MOME and PD are very small.

The increased NOx levels of MOME, JOME, RBME and SSME are also attributed to their higher viscosity. As viscosity increases, the fuel droplet size increases causing a lower evaporation rate. This lower evoparation rate increases ID, and hence the premixed combustion, which leads to the formation of thermal NOx.

The NOx emissions (at full load) of a diesel engine operating with biodiesel fuels are shown in Fig. 11, against the value of 580 ppm for petroleum diesel. This means, that NOx emissions with biodiesel combustion may increase or decrease, depending on the saturation/unsaturation of the biodiesel.

Despite the high CNs of fatty compounds (shown in Fig. 4), NOx emission increases slightly in DI diesel engine operating with some biodiesels. Also, as cetane number increases, NOx decreases. The NOx emissions are highest for SSME, which contains the highest percentage of polyunsaturated fatty esters, namely oleic methyl ester C18:1 and linoleic methyl ester C18:2.

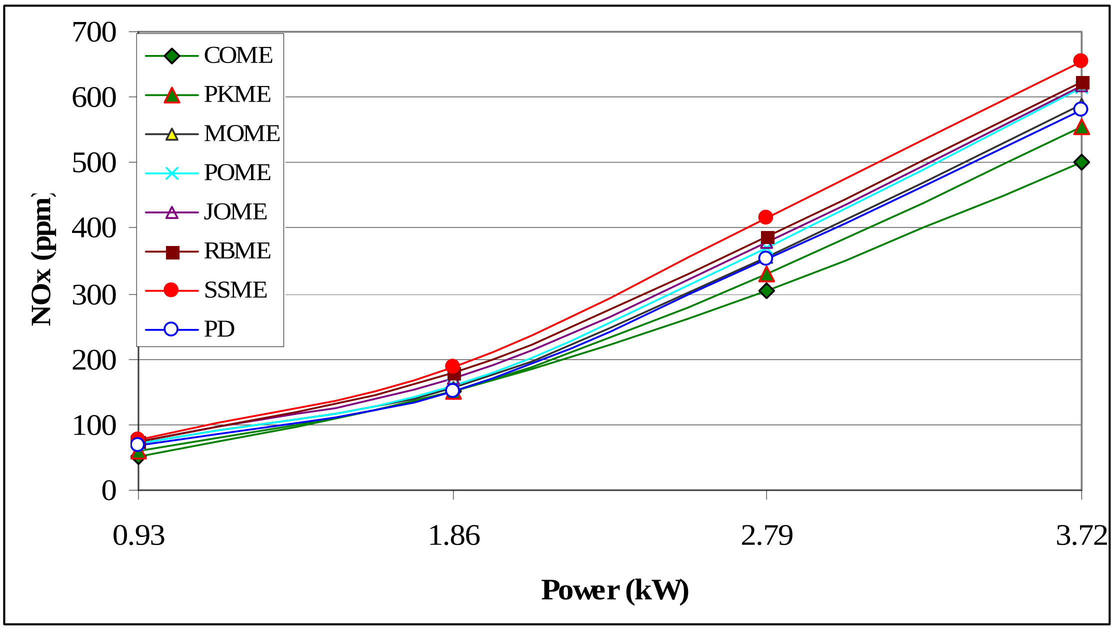


Fig.11: Variation of NOx (ppm) levels with respect to engine output power(kW)

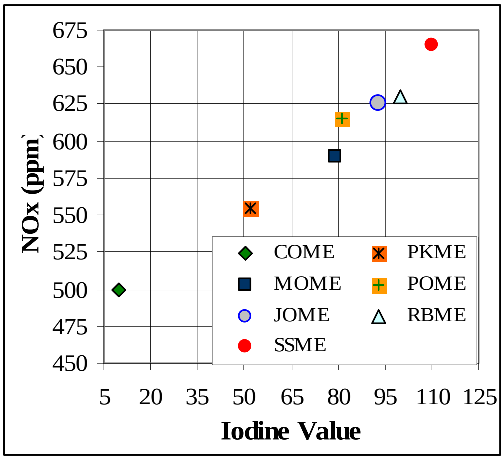


Fig.12: Iodine value vs. NOx (ppm) at 3.72 kW

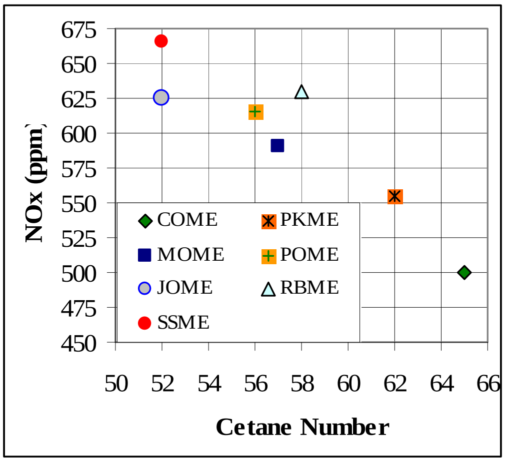


Fig.13: Cetane number vs. NOx (ppm) at 3.72 kW

Fig.12 shows the relationship between IV and NOx levels (ppm) of various biodiesel fuels: As iodine values increases, so do NOx emissions. COME which contains the least amount (9%) of unsaturated fatty acids produces the lowest NOx emissions (500 ppm), while SSME which contains the highest quantity (86%) of unsaturated fatty acids produces the highest (665 ppm). The high NOx emissions of SSME are due to the presence of more PUFA than in any of the other biodiesels tested (Fig. 2). Therefore, these data confirms the role of double bonds (particularly 18:2 and C18:3) in elevating exhaust NOx levels.

From Fig.4 and Fig.11, it is observed that NOx levels increase as branching increases, which can also lead to a connection with the CNs of fatty ester compounds. For example; the CNs of mono and polyunsaturated fatty acids (C18:1, C18:2 and C18:3) are lower than the CN of saturated fatty acid (C18:0) as shown in Fig.4. The biodiesel fuels (viz.: SSME, RBME, JOME, POME) containing more unsaturated fatty acids (MUFA and PUFA) are produce more NOx than other biodiesel fuels (viz.: COME and MOME) which contains more saturated fatty acids. Therefore, it is confirmed that the NOx levels increase with branching and as CN decreases as shown in Fig.13.

CONCLUSIONS

In order to investigate the combustion and NOx emissions of first and second generation biodiesel fuels, engine experiments were carried out at four different power outputs. From the experimental results, the conclusions drawn are as follows:

- As iodine value increases, the NOx increases
- The NOx emission of COME and PKME is lower than that of PD
- COME produces the lowest NOx emission and SSME the highest.
- Among the second generation biodiesel fuels, the NOx order is
  $(NOx)_{PKME} < (NOx)_{MOME} < (NOx)_{POME} < (NOx)_{JOME}$

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